

# Phonons Softening in Tip-Stretched Monatomic Nanowires

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## Abstract

It has been shown in recent experiments that electronic transport through a gold monatomic nanowire is dissipative above a threshold voltage due to excitation of phonons via the electron-phonon interaction. We address that data by computing, via density functional theory, the zone boundary longitudinal phonon frequency of a perfect monatomic nanowire during its mechanical elongation. The theoretical frequency that we find for an ideally strained nanowire is not compatible with experiment if a uniformly distributed stretch is assumed. With the help of a semi-empirical Au-Au potential, we model the realistic nanowire stretching as exerted by two tips. In this model we see that strain tends to concentrate in the junctions, so that the mean strain of the nanowire is roughly one half of the ideal value. With this reduced strain, the calculated phonon softening is in much better agreement with experiment.

Keywords : Nanowires, Gold, Conductance, Dissipation, Phonons, Softening.

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## 1 Introduction

Quantized electronic transport through metallic gold nanowires has been extensively studied experimentally [1]. Recent transmission electron microscopy and break junction data showed that unit conductance (in unit of  $G_0 = 2e^2/h$ )

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corresponds to tip-suspended wires segments consisting of a single monatomic strand [2,3,4]. At sufficiently low voltage, the conductance of these wires is ballistic. However, a recent experiment [5] showed that above a voltage threshold of about 15 meV a monatomic gold wire, seven atoms long, displays a drop of about 1 % in the differential conductance below the ballistic value of one. The symmetric drop of conductance with respect to the voltage sign and the value of the voltage threshold of around 15 meV suggested the effect to be due to inelastic scattering of electrons by longitudinal wire vibrations. Under that hypothesis, the voltage threshold yields precisely the frequency of the most important nanowire phonons. That voltage was shown experimentally to drop indicating a phonon softening with increasing stretching, and that needs to be quantitatively explained. Here we present calculations, based on density functional theory, of the vibrational frequencies of a monatomic gold wire and study their dependence on the wire stretching. Since simple arguments suggest that the phonon responsible for the effect is the longitudinal acoustic phonon at the zone boundary  $\pi/a$  ( $a$  is the gold-gold distance), we concentrate on the frequency of this vibration.

We show that the dependence of the longitudinal frequency on wire strain is not compatible with experiment if a uniformly distributed nominal strain is assumed. In order to analyze the role of possible non-uniform strain configurations, we modeled the mechanics of a realistic nanowire in contact with two tips with a semi-empirical gold potential. We found that strain was non-uniformly distributed, the tip-wire junctions absorbing a large fraction, and reducing correspondingly the true nanowire strain. With this reduction the agreement of experimental and theoretical stretch-dependent phonon frequency was very much improved.

## 2 Phonon Calculations for a Stretched Nanowire

We considered an infinite monatomic nanowire and calculated its phonon frequencies as a function of the wire strain, that is for increasing interatomic spacing  $a$ . The model is of course very crude since it does not include at all the wire-tip junctions; but as a simple approximation it allows us to address first of all the reduced dimensionality effect on the force constants among gold atoms. The nanowire total energy and electronic structure were deter-

mined within standard Density Functional Theory (DFT) in the local density approximation. The phonon frequencies were calculated within density functional perturbation theory, using the PWSCF and PHONON codes [6] with the gold pseudopotential of Ref. [7]. The gold wire was simulated by using a tetragonal periodically repeated supercell. The wire was oriented along the  $z$  axis and repeated periodically along  $x$  and  $y$  with a wire-wire distance (10.58 Å) large enough to avoid unphysical interactions among replicas. The energy cutoffs of the plane wave basis was 28 Ry for the wavefunctions and 252 Ry for the charge density. We used 40 uniformly distributed  $\mathbf{k}$  points to integrate the one dimensional Brillouin zone and a broadening technique [8] with a smearing parameter of 0.01 Ry to deal with the presence of a Fermi level. These parameters were found to be sufficient for a good convergence of the results. Based on these first principles calculations, we also generated parameters for an empirical effective potential between gold atoms. In a tight binding scheme, and in the second moment approximation (SMA), the effective potential between Au atoms separated by  $r_{ij}$  may be written as [9]:

$$E_i = \lambda \sum_j e^{-p\left(\frac{r_{ij}}{r_0}-1\right)} - \epsilon \left( \sum_j e^{-2q\left(\frac{r_{ij}}{r_0}-1\right)} \right)^\alpha \quad \text{with } r_{ij} < r_c \quad (1)$$

The parameters entering in the above expression can be obtained by fitting the first-principles energies and related bulk properties of gold. We obtain in this way  $\lambda = 0.4086$ ,  $p = 8.5624$ ,  $\epsilon = 1.6332$ ,  $q = 3.6586$ ,  $\alpha = 0.6666$ ,  $r_0 = 2.88$  Å.

### 3 Results and discussion

In our first step, we calculated with DFT the equilibrium properties of the infinite monatomic wire (Fig. 1). The stable chain under zero tension (minimum of the total energy) has a nearest neighbour distance  $a_0=2.49$  Å in agreement with other calculations [10,11,12]. Neglecting electron reflection at the junctions (justified for a very wide s-band) this ideal wire has a ballistic conductance of one due to a single band crossing the Fermi level at  $\pi/2a_0$ . The important resistive electron-phonon coupling is electron backscattering by the zone boundary longitudinal phonon at  $q_z = \pi/a_0$ . At the strain-free equilibrium spacing  $a_0$ , the calculated phonon frequencies are 240 cm<sup>-1</sup> and

152  $\text{cm}^{-1}$  for the longitudinal and the two degenerate transverse modes, respectively. As a reference, with these pseudopotentials, the stretch frequency of the Au dimer is  $191 \text{ cm}^{-1}$ . The imaginary frequency of transverse modes indicates that an infinite wire is unstable under zero tension, for example against a zigzag distortion, as discussed in Ref.[12]. This in no way implies that the real wire segment hanging between the two tips will be distorted, since the equilibrium geometry will be strongly influenced by the tips. In particular, grand canonical tip-wire equilibrium requires a positive string tension [7], and an increase of  $a$ . We find that the frequency of the transverse modes becomes positive for  $a=2.75 \text{ \AA}$ .

Returning to the evolution of the frequency of the longitudinal phonon under wire stretching, we calculated that by increasing progressively the distance between atoms in the chain. We show in Fig. 2 the evolution of the vibrational frequency  $\omega_X$  at the  $X$  point as a function of the distance  $a$ . During stretching the bond softens and  $\omega_X$  decreases almost linearly as  $a$  increases. At  $a=2.85 \text{ \AA}$ ,  $\omega_X$  becomes negative and above this distance the infinite wire is unstable, for example against dimerization. For comparison, we also plotted in Fig. 2 the frequencies deduced from the experiment of Ref. [5] (long dashed line). In order to decide the position of these points we made two assumptions. First we converted the measured elongation,  $0.75 \text{ \AA}$ , into an elongation of the gold-gold bonds, assuming that the experimental wire is uniformly stretched and dividing the total elongation on each bond of the 7 atom wire. Next we had to decide what was the starting gold-gold distance in the experimental curve. Since the initial wire tension is unknown, we assumed the highest measured longitudinal frequency to correspond to a bond length equal to  $2.68 \text{ \AA}$ . In this way the experimental and theoretical frequencies of the first point coincide. The slopes of the two curves however differ by a factor of almost 2, theory decreasing faster than experiment.

This discrepancy between the calculated dependence of the longitudinal frequency on the gold-gold distance and the measured one is too large to be attributed to computational inaccuracy, and rather suggests that we made a wrong assumption somewhere. Our main doubt eventually converged on the assumption of uniform strain. On the one hand the gold-gold bond could be expected to be stronger in the monatomic nanowire than in the tip, as indicated by shorter distances. On the other hand the dependence of the experimental phonon frequency with strain would be in better agreement with the theoret-

ical values if one were to assume a elongation of  $0.04 \text{ \AA}$  instead of nearly  $0.1 \text{ \AA}$  (7 Au atoms and a total elongation of  $0.75 \text{ \AA}$ ).

A full ab-initio attack of this problem is desirable but seems well beyond the scope of our work. Thus, we investigated further this aspect by simulating with our classical SMA effective potential a realistic 7-atom chain in contact with two tips, where all atoms in the chain and in the tips are allowed to move without any geometrical constraints. It is important to note that the mechanical properties of the gold wire calculated by DFT and SMA differ by very little, essentially only a small shift of the equilibrium spacing (about  $0.05 \text{ \AA}$ ) and the cohesive energies differs by only  $0.23 \text{ eV}$  (see Fig. 1). The gold chain is thus obtained by optimizing the total energy of the atoms in the system while the distance of the two tips is increased. Each step corresponds to an elongation of  $0.02 \text{ \AA}$ . At each step, the equilibrium configuration attained is only guaranteed to be a local minimum of the potential energy surface, which in turn depends on the starting configuration. Nevertheless, the strain evolution obtained appeared very reasonable, providing a vivid picture of a possible inhomogeneous strain in the tip-suspended nanowire.

Fig. 3 displays typical snapshots during the formation and the stretching of a wire. At the beginning of the stretching (Fig. 3a), the two tips are stuck together. Upon stretching a twisted chain appears while one atom is extracted. Subsequently a chain of 8 atoms is formed by successive incorporation of atoms from the tips. At this length, the simulated nanowire broke. Incorporation of each new atom in the chain was observed after a elongation of nearly  $1.5 \text{ \AA}$  and involved a sudden downward jump in bond lengths. This crude model shows that the wire of given length can only be stretched elastically over a limited distance which compares well with the  $1 \text{ \AA}$  in the experiments [5]. The calculated change of nanowire interatomic distance for a total elongation tip-tip distance of  $0.75 \text{ \AA}$  and a chain of 7 atoms was  $0.03 \text{ \AA}$ , instead of nearly  $0.1 \text{ \AA}$  as expected the perfect chain. Using a nanowire strain corrected by this scaling factor, the experimental phonon softening against corrected strain (dot-dashed line in figure 2) is now in much better agreement with theory.

## 4 Conclusion

We calculated the evolution with stretching of the longitudinal phonon frequency of a monatomic gold wire, motivated by recent observations indicating a softening. The softening obtained via density functional theory in a monatomic wire is indeed large, in fact too large. It is compatible with the experimental data only if a non uniform distribution of the strain is introduced, the largest strain being taken up by the tips and tip-wire junctions, and only 40% of the strain in the chain.

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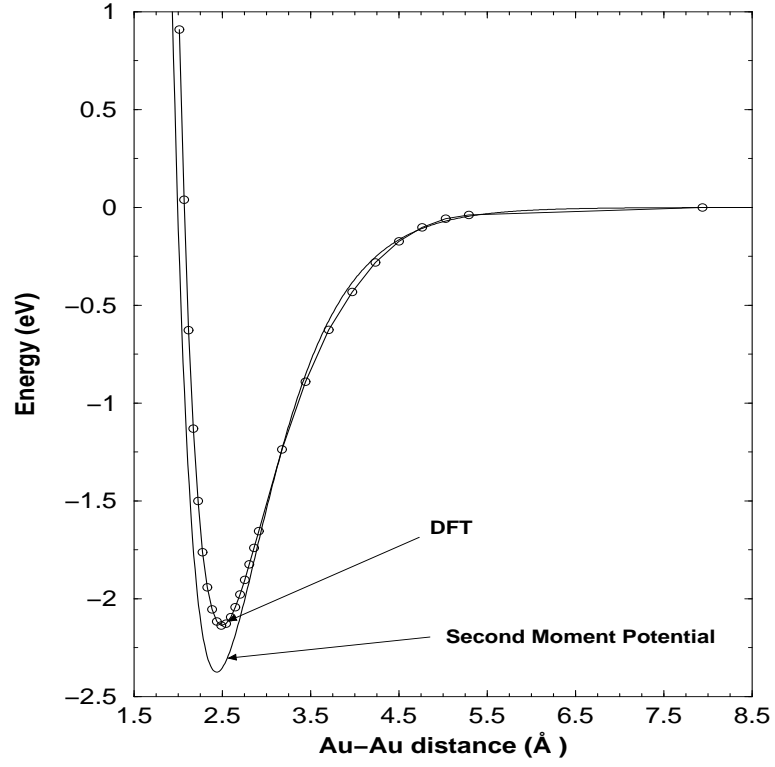


Fig. 1: Circles and continuous line: total energy of the infinite monatomic gold wire obtained by DFT-LDA as a function of the Au-Au distance. Dashed line: total energy of the infinite monatomic gold wire calculated with the semi-empirical potential[9].



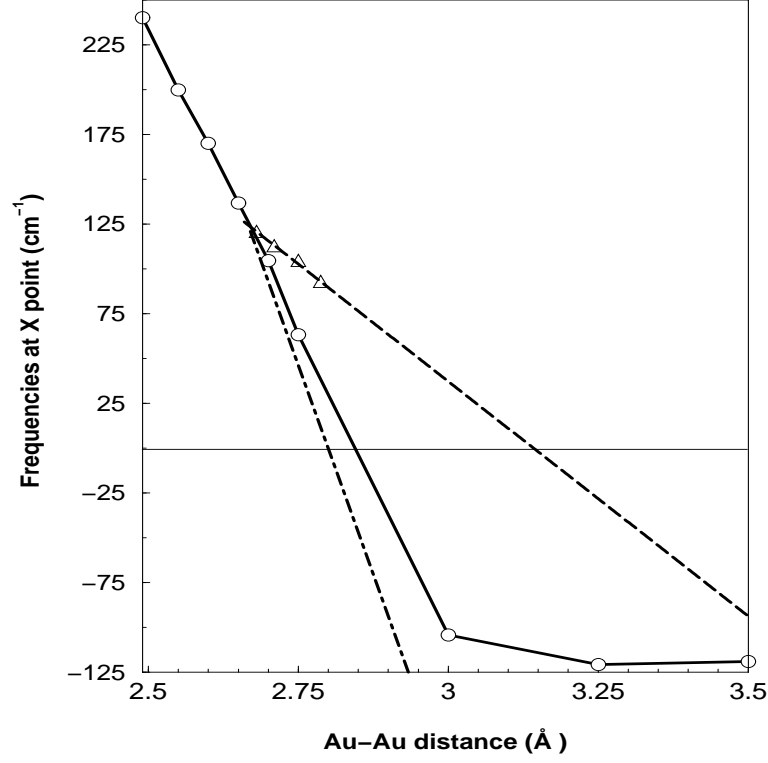


Fig. 2: Frequencies of the longitudinal phonon as a function of the gold-gold distance. Continuous line and circles correspond to theoretical results. Triangles are the experimental data in the first linear part of Fig. 3d of Ref.[5]. The dashed line is a linear interpolation of experimental data. The dot-dashed line represents the experimental frequencies replotted for a stretching rescaled by a factor 0.3 (see text).

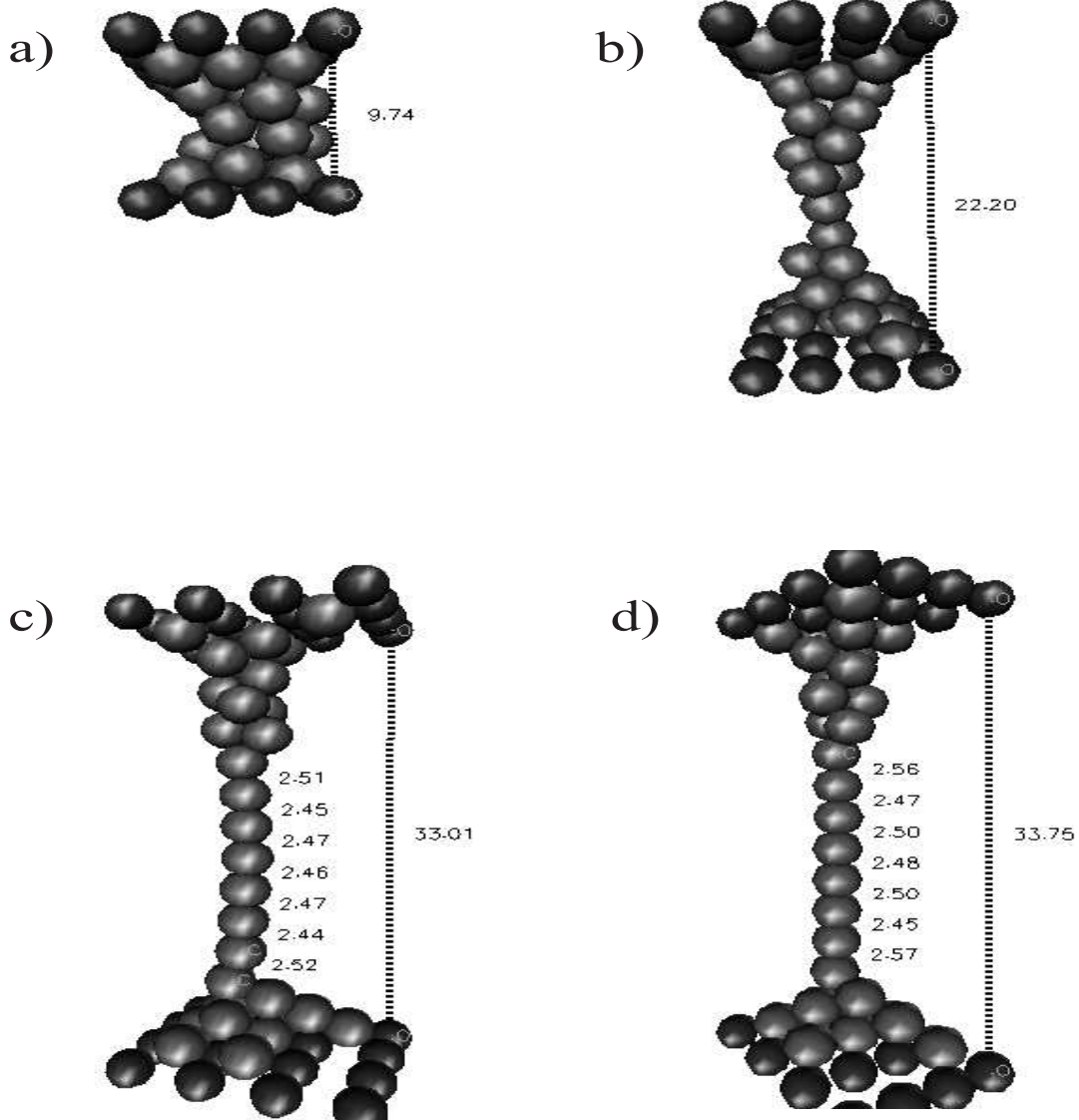


Fig. 3: Mechanical model. The total energy of the system is minimized during the stretching of the two tips. a) Starting configuration of the simulation. The two tips are in the nearest position. b) One atom is extracted . c) Strained nanowire 7 atoms long. The lengths of each bond are indicated on the snapshot. d) After elongation of  $0.75 \text{ \AA}$  of the 7 atoms wire, one supplementary atom is extracted. At this moment, the evolution of the bonds shows a mean deviation of  $0.03 \text{ \AA}$ . The wire broke in this simulation before extraction of the 9th atom.